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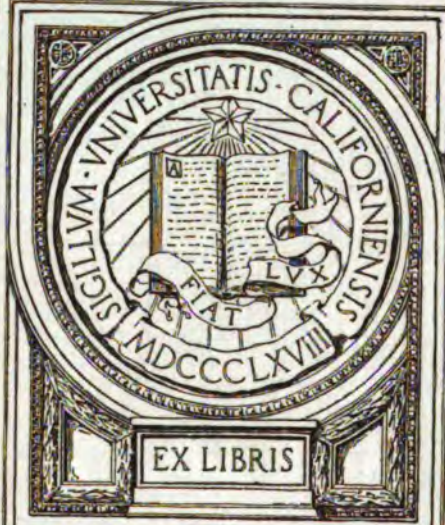
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# A LEAD STANDARD CELL AND A DETER- MINATION OF THE POTENTIAL OF THE LEAD ELECTRODE

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## DISSERTATION

PRESENTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE  
OF DOCTOR OF PHILOSOPHY IN THE GRADUATE SCHOOL OF  
THE OHIO STATE UNIVERSITY



BY

GEBHARD STEGEMAN

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**A LEAD STANDARD CELL AND A DETERMINATION OF THE POTENTIAL  
OF THE LEAD ELECTRODE.**

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## I. Reason for the Investigation.

A series of investigations has been in progress in this laboratory for some time, having for its object a study of the applicability of the measurement of electromotive force to the determination of the transition temperatures of hydrated salts.

This method first suggested by Callender and Barnes,<sup>1</sup> and later developed by Geiger,<sup>2</sup> depends upon the change in slope of the solubility curve of a salt accompanying the change from one hydrate to another. Since the electromotive force of a cell in which the hydrated salt comprises a part is a function of the solubility of the salt, any change in the solubility curve of that salt will have a noticeable effect upon the electromotive force. If the electromotive force of such a cell is plotted against the temperature, the slope of the curve obtained will undergo a change at the transition temperature of the salt, and by measuring the electromotive force at different temperatures the transition temperature of the salt may be determined. For example, in the Clark cell, the salt which is stable up to  $38.2^{\circ}$  is zinc sulfate heptahydrate ( $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ). This salt changes to the hexahydrate ( $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ ) at  $38.2^{\circ}$ , and since at this temperature both salts have the same solubility, the voltages of two cells containing, respectively, the heptahydrate and the hexahydrate would be identical. At no other temperature would this condition prevail. The fact that salts frequently remain in a metastable condition beyond the transition temperature does not affect the accuracy of the method, since by plotting the electromotive force against the temperature two curves are obtained depending upon which salt is present in the cell, and the point of intersection of the two curves, representing the point of equal solubility will be the transition temperature.

A cell used in the determination of the transition temperature of the salt comprising a part of that cell, must have the negative electrode composed of some metal which does not decompose water to an extent sufficient to affect the constancy of the electromotive force. The metals used in such cells have been chiefly zinc and cadmium, and the electrode must in general liberate an ion similar to that liberated by the salt in question. This requirement has prevented the determination of the transition temperature of a salt such as sodium sulfate decahydrate ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ), since a sodium electrode would decompose water so readily, that it would not show a constant electromotive force. The same type of cell which would allow a determination of the transition temperature of a salt such

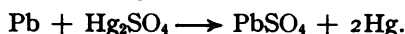


as zinc sulfate heptahydrate, could, therefore, not be used in the determination of the transition temperature of sodium sulfate decahydrate ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ).

In the hope of finding a type of cell which would avoid these difficulties and still permit the determination of the transition temperature of a salt such as sodium sulfate decahydrate,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , the following type of cell was prepared:



The chemical reaction occurring in the cell is



This reaction does not show that the sodium sulfate is in any way connected with the reaction, but the electromotive force of such a cell is a function of the solubility of the lead sulfate ( $\text{PbSO}_4$ ), and this is in turn dependent upon the amount of sodium sulfate in the solution. It was thought that the mass effect of the common ion  $\text{SO}_4$  would cause sufficient change in the amount of lead sulfate dissolved to make a perceptible change in the electromotive force. Thus by raising the temperature of the cell and thereby increasing the amount of sodium sulfate in solution, a subsequent decrease in the amount of the lead sulfate dissolved should cause a change in the electromotive force. At the transition temperature of the sodium sulfate, the solubility of the hydrated salt is the same as the solubility of the anhydrous salt, and consequently the electromotive force of the cell should have a definite value no matter which salt is present.

It is essential for accurate determinations of the transition temperatures of salts by this method that the temperature coefficient of the cell be rather large. Reference to Table I will show that the temperature coefficient of a cell made with an unsaturated amalgam is very small and for this reason the study of these cells with reference to the transition temperatures of salts was discontinued. The freedom from variation of the electromotive force of this type of cell suggested further study with the following aims:

(1) The determination of the condition under which the cell would be reproducible.

(2) The use of the cell as an indirect method to determine the potential of the lead electrode.

(1) It was found that the lead amalgam used was an unsaturated one, that is, the percentage of lead was below that required to saturate the mercury with lead. Lead is soluble in mercury to the extent of

about 1.5% by weight and any attempt to dissolve more lead in the mercury results in the formation of the compound ( $\text{Pb}_2\text{Hg}$ ). This compound is in equilibrium with a saturated amalgam. The active part of the electrode is the liquid amalgam and any decrease in the percentage of lead during the action of the cell is compensated by the solution of the compound ( $\text{Pb}_2\text{Hg}$ ), which tends to restore the previously existing equilibrium.

In order to make a lead electrode with a reproducible electromotive force, a saturated amalgam is obviously the concentration to be sought, and this concentration may be obtained by having an excess of the compound  $\text{Pb}_2\text{Hg}$  present at all times. From a study of the electromotive force of lead amalgams, Puschin<sup>3</sup> has concluded that the potential of such amalgams has a constant value when the concentration of lead is between the limits of 1.8 and 66%. An electrode consisting of lead and mercury with the lead concentration between these limits should, therefore, be reproducible, and a study of the most convenient concentration which would give a reproducible electromotive force was undertaken.

## II. Preparation of Materials.

(1) Lead nitrate. A sample of Baker's C. P. lead nitrate was twice recrystallized from pure water and served as the source of lead for the amalgams.

(2) Lead amalgams. The amalgams were prepared in two ways:

(a) A solution of lead nitrate, containing a trace of nitric acid and about 10% of lead nitrate, was electrolyzed in a platinum dish which served as the cathode, with a thin plate of platinum foil serving as the anode. The current used was never more than one-tenth of an ampere while the voltage was one and one-half volts. The precipitated lead was washed with water while adhering to the dish and was readily removed. To dry the crystals completely they were washed with a solution of alcohol-ether and the last traces of the liquid were removed by a clean blast of dry air. The dry crystals were then melted in a hard glass flask in an atmosphere of hydrogen to prevent oxidation. The metallic button thus obtained was preserved for use in the preparation of the amalgams.

Suitable quantities of lead and mercury were weighed in porcelain crucibles and the lead which was cut into small pieces was added to the mercury. The crucible was then warmed somewhat to promote the solution of the lead and the amalgam formed was stirred with a glass

rod till it appeared to be homogeneous. To prevent undue oxidation during the heating, the amalgam was protected by a coating of liquid paraffin. When the amalgam was to be transferred to the cell, the thin coating of paraffin was removed with a spatula, and the amalgam was placed in the cell by means of a small-bore pipette since the amalgam is liquid when warm. Upon cooling a granular compound separates out, which has been shown by Fay and North<sup>4</sup> to have the composition  $\text{Pb}_2\text{Hg}$ . They have also shown that this compound exists in equilibrium with the liquid part of the amalgam even though the percentage of lead vary from two to fifty-five per cent. When this equilibrium has been established the liquid and the solid phase have the same potential which should, therefore, be constant within these limits at any one temperature.

(b) The amalgam was also prepared electrolytically by the electrolysis of a ten percent solution of lead nitrate with a weighed amount of mercury serving as the cathode. A coulometer in the circuit served to show the amount of lead deposited in the mercury. When the electrolysis had proceeded to the desired point, the solution of lead nitrate was decanted from the amalgam which was then thoroughly washed with distilled water. There seems to be little to choose between the two methods as both produce amalgams of identical voltages. The electrolytic method is perhaps the more convenient of the two, since it is easily controlled and is not attended by any oxidation such as is likely to occur when a lead amalgam is heated.

(2) Sodium sulfate ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ).

A supply of C. P. anhydrous sodium sulfate was dissolved in pure distilled water and the crystals of sodium sulfate formed were twice recrystallized. The salt was kept in a slightly moistened condition to prevent efflorescence. The presence of a trace of ferric ion present in the original salt could not be detected after the second recrystallization.

(3) Mercurous sulfate ( $\text{Hg}_2\text{SO}_4$ ).

The preparation of this very important compound was carried out with the greatest attention possible. The method employed by Hulett<sup>5</sup>, an authority on the construction of standard cells, was carefully followed. This consists in electrolyzing a solution of sulfuric acid of specific gravity 1.15, in a glass dish with an anode of pure mercury. This method has the distinct advantage that the precipitated mercurous sulfate is very intimately mixed with minute globules of mercury. This intimate mixture of salt and metal is a protection against the formation of any mercuric salt, since the metallic mercury acts as a very effective reducing agent. The presence of mercuric salts must be avoided since they are so much more soluble than the mercurous salts and the potential existing between the mercury

and a solution of its salts, depends upon the concentration of mercury ions. The salt prepared by this method was preserved in a dark colored bottle under the solution from which it was prepared.

(4) Lead Sulfate:

This salt was prepared by precipitation from a dilute solution of lead nitrate by means of dilute sulfuric acid. In order to remove any occluded lead nitrate, the precipitate was boiled four times with successive portions of distilled water which was decanted after the precipitate had settled. This salt was kept in a glass-stoppered bottle under dilute sulfuric acid to prevent the hydrolysis which might occur if kept in contact with pure water.

(5) Mercury:

Ordinary mercury was stirred for two days in contact with dilute nitric acid, and was then distilled under reduced pressure according to the method of Hulett.<sup>6</sup> After the second distillation no oxides of any kind remained either in the distilling flask or the receiver. The mercury thus purified maintained its mirror surface indefinitely.

(6) The Paste:

The mercurous sulfate prepared as described was washed until free from the acid under which it was preserved. This was very conveniently done in a Gooch crucible with a small disk of filter paper accurately fitting the bottom. The mercurous sulfate was poured into the crucible and the acid drawn off by suction. The acid remaining upon the salt was removed by five or six small portions of a saturated solution of sodium sulfate. Each portion of the washing solution was removed as completely as possible by suction before adding a new portion. This kind of procedure prevents the troublesome hydrolysis of the mercurous sulfate which occurs in aqueous solution according to the following equation:



This hydrolysis must be avoided as the acid produced has a marked effect upon the potential difference existing between the mercury and the solution of mercurous sulfate.

The lead sulfate prepared according to the previous description was washed free from the acid under which it was kept, in a way analogous to that described in the case of the mercurous sulfate. A mixture consisting of equal portions of mercurous sulfate, lead sulfate, and sodium sulfate, was stirred till it appeared well mixed and enough of a saturated solution of sodium sulfate was added to make a thin paste.

(7) Preparation of the Cell:

The H type of cell appeared to be the best adapted to the work contemplated. The glass part of the cell was prepared by joining together two "culture-tubes" such as are used in bacteriological work at about four cms. from the closed end. The glass of which these tubes are made is easy "to work" and does not crack on cooling. Two small-bore glass tubes with platinum wires sealed into one end passed through the stoppers placed in the open ends of the cell, and served to connect the cell with the potentiometer.

When the cell was ready to be filled, some of the pure distilled mercury was placed in one leg of the glass vessel by means of a small-bore pipette. Some of the paste consisting of an intimate mixture of mercurous sulfate, lead sulfate, and sodium sulfate was then placed upon the mercury to a depth of about one cm., also by means of the pipette. The lead amalgam was then placed in the other leg of the cell in a similar manner. Most of the amalgams used were liquid with a small amount of the solid phase in equilibrium with it. By warming this amalgam slightly, the solid phase readily dissolved in the liquid phase and was then easily placed in the cell as a homogeneous liquid. Upon cooling, the solid phase again separated out so that a saturated amalgam was always present. In the case of amalgams containing a higher percentage of lead, the pipette used to transfer the amalgam from the container to the cell was warmed in the Bunsen flame, and the warm amalgam was drawn into it. Before the temperature had fallen to the solidification point, the amalgam was quickly placed in the cell. In this way only the pure amalgam containing no oxide was transferred to the cell. This amalgam was then covered immediately with a mixture consisting of solid lead sulfate intimately mixed with finely powdered sodium sulfate. This mixture was made into a thin paste by adding a little water saturated with both lead sulfate and sodium sulfate. The cell was then filled up to the cross arm with an intimate mixture of both lead sulfate and sodium sulfate. Enough of a solution saturated with both these salts was then added so as to fill the cell above the cross arm. The glass leads containing the platinum wires were then placed in position, and cork stoppers provided with a hole for the glass tubes placed in the ends of the tubes. Two or three such cells were then tied in a bundle and took up but little room in the thermostat.

### III. Apparatus.

#### (a) *Thermostat.*

Two thermostats electrically heated and regulated to  $0.01^{\circ}$  were available and served to keep the cells at any desired temperature. One of

these thermostats was regulated at  $25.00^{\circ}$  and the Weston cell serving as a reference was always kept at this temperature.

(b) *Thermometer.*

The thermometer was graduated in tenths of a degree and had been standardized by the Bureau of Standards at Washington. By the aid of a small eye-glass the temperature could be accurately read to one-hundredth of a degree.

(c) *Standard Cell.*

The Standard Cell was of the Weston unsaturated type procured from the Weston Laboratory. The one used for constant reference was No. 3,408 and had a voltage of 1.01865 volts at  $25^{\circ}\text{C}$ . It was frequently compared with a similar cell, No. 3,539, which was recently procured. It was constantly kept in the thermostat regulated at  $25.00^{\circ}$ .

(d) *Potentiometer.*

The potentiometer used to measure the voltages of the cells was a Leeds and Northrup instrument reading to 0.00001 volt.

(e) *Galvanometer.*

A very sensitive Leeds and Northrup galvanometer was employed as a "Null instrument." This instrument was sensitive enough to detect a change of less than 0.00001 volt.

(f) *Battery.*

The source of current for the potentiometer was an ordinary "chloride accumulator" showing a voltage of about 2.10 volts.

## IV. Results.

(a) Observations on cells prepared with unsaturated lead amalgams.

(b) Observations on cells prepared with saturated amalgams.

(a) All cells prepared according to the manner described were allowed to remain in the thermostat for about twelve hours before any readings were recorded. The first type of cell studied was prepared with an unsaturated lead amalgam as the negative electrode and contained approximately 0.70% of lead. Since this percentage is below the saturation point of lead in mercury, the observed electromotive force is a function of the concentration of the lead in the amalgam. This type of cell exhibited some interesting features, however, namely, the constancy of voltage and the low temperature coefficient.

TABLE I.

Observation on a Cell with a 0.703% Pb Amalgam.

E. M. F.	Time.	Temp.
0.95815	11/15/16	25.00°
0.95815	11/22/16	25.00°
0.95820	11/23/16	30.00°
0.95820	12/ 5/16	30.00°

This type of cell has a temperature coefficient of  $+0.00001$  volt. It is also interesting to note that the voltage increases with rise of temperature, a property possessed by few voltaic cells, the most prominent one being the Daniel cell.

Since these cells exhibit such a constant voltage it was interesting to see how well the observed values of voltage and temperature coefficient would agree with the theoretical value. The Gibbs-Helmholtz equation connects the heat of reaction of a cell with the electromotive force as follows:

$$Q = NF(E - TdE/dT)0.2387$$

In this equation  $Q$  = heat of reaction determined from thermochemical data.

0.2387 is the conversion factor for electrical to heat energy

$E$  is the observed electromotive force.

$T$  is the absolute temperature.

$dE/dT$  is the temperature coefficient.

$N$  is the valence of the reacting metal.

$F$  is one Faraday or 96,550 coulombs.

The reaction taking place in the cell is given by the equation  $Pb + Hg_2SO_4 \rightarrow PbSO_4 + 2Hg$ . The reaction in this cell is very simple, and in making a comparison between observed and calculated values, no complication is introduced, due to the heat of hydration of the salt formed, as is the case in the Clark and Weston cell. The heat of formation of lead sulfate from its elements at  $18^\circ$  as determined by Thomsen is 216,200 cal. The heat of formation of mercurous sulfate is given as 175,000 cal. The difference 41,200 cal. represents the heat liberated in the reaction. The heat of the reaction as determined by the Gibbs-Helmholtz equation is as follows: At  $18.00^\circ$  the e. m. f. of the cell under consideration is 0.95808 and  $dE/dT = +0.00001$ .

Therefore,  $Q = NF[0.95805 - 291(0.00001)]0.2387 = 44,025$  cal.

However, the reaction occurring in the cell is not wholly represented by  $Pb + Hg_2SO_4 \rightarrow PbSO_4 + 2Hg$ , but is instead,  $Pb\text{-amalgam} + Hg_2SO_4 \rightarrow PbSO_4 + 2Hg$ .



Bronsted<sup>7</sup> has shown that a chain [Pb solid—Pb salt—Pb 0.72% amalgam] gives a voltage ( $0.0051 + 0.000233t$ ).

Substitution of these values in the Gibbs-Helmholtz equation gives a value of  $-2,697$  cal. for the heat of solution of Pb in mercury to form a 0.72% amalgam at  $18.00^\circ$ .

$$Q = 0.2387[0.0092 - 291(0.000233)]NF = -2,697 \text{ cal.}$$

When a cell containing a lead electrode composed of an unsaturated amalgam of 0.72% Pb is in action, 2,697 cal. of heat will be liberated for every atomic weight of lead going into solution.  $44,025 - 2,697 = 41,328$  cal. would, therefore, be the free energy of the reaction as compared with 41,200 cal. obtained in a thermochemical way.

Attention was next directed toward a verification of the assertion that between certain limits of concentration the potential of lead amalgams is independent of the concentration of lead. As before mentioned, Puschin<sup>8</sup> has shown that amalgams of lead have the same potential between the limits of 1.8–66% of lead. Several cells were prepared with amalgams varying in concentration from 2 to 10% of lead, 10% being about the limit for convenient handling since amalgams with a higher percentage of lead are quite solid at ordinary temperatures. The best results so far obtained have been with amalgams ranging from a percentage of lead of 2.5 to 3.9% as shown by the following table:

TABLE II.

Cell I Amalgam 2.6% Pb.	Cell II Amalgam 3.5% Pb.	Time.	Temp.
0.96470	0.96453	Dec. 12, 1916	25.00°
0.96465	0.96470	Jan. 18, 1917	25.00°
0.96465	0.96468	Feb. 2, 1917	25.00°
0.96463	0.96464	Mar. 2, 1917	25.00°
0.96463	0.96464	Apr. 6, 1917	25.00°
0.96342	0.96343	Apr. 15, 1917	18.00°
0.96343	0.96343	Apr. 18, 1917	18.00°
0.96550	0.96552	Apr. 19, 1917	30.00°
0.96550	0.96552	Apr. 21, 1917	30.00°
0.96463	0.96463	May 15, 1917	25.00°

While these cells have different concentrations of lead in the amalgams, and did not agree well at first, they have both assumed the same value, and appear to remain so except for a very gradual decrease in voltage, a property often encountered in such good cells as the cadmium standard cell.

To test the reproducibility of these cells, three cells were prepared on Feb. 9, 1917, in the usual way with the exception that the amalgams were prepared electrolytically. The voltages obtained follow:

TABLE III.

Cell I.	Cell II.	Cell III.	Temp.	% of lead in amalgam.	Date.
0.96465	0.96461	0.96464	25.00°	3.10%	2/12/17
0.96465	0.96462	0.96463	25.00°	..	2/15/17
0.96465	0.96462	0.96463	25.00°	..	2/18/17
0.96464	0.96461	0.96462	25.00°	..	3/12/17

A comparison with the other two cells described shows that all five cells have the same voltage within a few hundredths of a millivolt, thus making the cell reproducible within that limit. Since the cell shows a voltage that is quite constant and appears to be reproducible to a few hundredths of a millivolt, it is possible to make a determination of the free energy of the reaction occurring in the cell using the values that have been determined as a basis. As previously indicated, this may be done by means of the Gibbs-Helmholtz equation:

$$Q = NF(E - TdE/dT)0.2387$$

A very careful determination of the value  $dE/dT$  is necessary for an accurate determination of the value of  $Q$ . The great accuracy required in this operation will be evident from a consideration of the equation. The factor  $dE/dT$  is multiplied by the absolute temperature  $T$ , in this case 291, and the effect of a small error in the value of  $dE/dT$  is thus considerable. To determine the value  $dE/dT$ , we may proceed as follows: The electromotive force at any temperature may be expressed as a function of the value of the electromotive force at any given temperature. Thus we may write,

$$E_T = E_{25} + a(T - 25) + b(T - 25)^2. \quad (I)$$

The last term in the equation is necessary because the variation of the electromotive force with the temperature is not always a straight line function. Referring to equation (I), it is evident that it consists of an equation with two unknown quantities, "a" and "b." To evaluate these constants it is necessary to know the value of the electromotive force at three different temperatures. There will then be two simultaneous equations from which the value of the constants may be determined. The temperatures chosen for observation were 30, 25 and 18°. Table II gives the values obtained at these three temperatures, and a substitution of these values in equation (I), gives two simultaneous equations of the following form:

$$0.96343 = 0.96463 + a(-7) + b(49)$$

$$0.96551 = 0.96463 + a(5) + b(25)$$

The solution of these two simultaneous equations gives a value of  $+0.000174$  for "a" while "b" has the value  $+0.00000038$ . Equation (I) then assumes the form:

$$E_T = 0.96463 + 0.000174(T - 25) + 0.00000038(T - 25)^2$$

This equation reproduces the values found at 30 and 18°, and by differentiating this equation the value for  $dE/dT$  at 18.00° is found to be  $+0.000169$ . Substitution of the values found in the Gibbs-Helmholtz equation gives the equation the following form:

$$Q = 46092[0.96343 - 291(0.000169)] = 42,139 \text{ cal.}$$

However, the reaction occurring in the cell is not wholly represented by  $\text{Pb} + \text{Hg}_2\text{SO}_4 \rightarrow \text{PbSO}_4 + 2\text{Hg}$ , but by  $\frac{1}{2}\text{Pb}_2\text{Hg} + \text{Hg}_2\text{SO}_4 \rightarrow \text{PbSO}_4 + 2\frac{1}{2}\text{Hg}$ . The heat of solution of lead in mercury to form the compound  $\text{Pb}_2\text{Hg}$  must, therefore, be determined before the actual heat of the reaction occurring in the cell can be determined. Bronsted<sup>7</sup> has determined the electromotive force of a chain  $[\text{Pb}_{\text{solid}} - \text{PbCl}_2 - \text{PbHg}_{137}]$  and has found it to be  $(0.0051 + 0.000233t)$  volt. These values when substituted in the Gibbs-Helmholtz equation give a value of  $-2,697$  cal. as the heat of solution of lead in mercury to form a dilute amalgam as previously indicated. The amalgam used in the cell under consideration consists of the compound  $\text{Pb}_2\text{Hg}$  in equilibrium with a saturated amalgam and the heat of reaction when lead dissolves to form this compound would not be the same as that occurring when lead goes to form a dilute amalgam. The heat of reaction when the compound  $\text{Pb}_2\text{Hg}$  is formed was determined indirectly by Luther.<sup>8</sup> The chain  $[\text{Pb}_2\text{Hg} - \text{PbCl}_2 - \text{PbHg} \text{ dilute amalgam}]$  was found to give an e. m. f.  $(0.00016 + 0.000191t)$ . At 18° the heat of reaction calculated from the Gibbs-Helmholtz equation is  $-2,115$  cal. The difference between  $(-2,697$  and  $-2,115)$  amounting to  $-582$  cal. must be the heat of reaction when lead dissolves in mercury to form the compound  $\text{Pb}_2\text{Hg}$ . The value of the heat of reaction occurring in the cell under consideration will be too high by this amount, and the true value for the reaction  $\text{Pb} + \text{Hg}_2\text{SO}_4 \rightarrow \text{PbSO}_4 + 2\text{Hg}$  will be  $41,557$  cal., against  $41,200$  cal. obtained thermochemically. This is an error of approximately 0.86%, almost as good an agreement as found in the Clark cell.

It appeared interesting to try the effect of the substitution of zinc sulfate heptahydrate for the sodium sulfate decahydrate in the cell. Some cells were accordingly prepared in the same way as that described with the exception that zinc sulfate was used instead of sodium sulfate throughout. The values obtained follow:

TABLE IV.

Cell I.	Cell II.	Date.	Temp.
0.96487	0.96485	3/ 6/17	25.00°
0.96487	0.96485	3/12/17	25.00°
0.96487	0.96485	3/15/17	25.00°
0.96364	0.96362	3/16/17	18.00°
0.96364	0.96362	3/18/17	18.00°
0.96563	0.96561	3/19/17	30.00°
0.96563	0.96561	3/20/17	30.00°
0.96487	0.96485	3/28/17	25.00°

It is interesting to note that in spite of the larger solubility of the zinc sulfate the voltage of a cell prepared in this way is only 0.00023 volt higher than that of a cell in which sodium sulfate is used. The voltage of this cell at any temperature may be calculated by means of the equation:

$$E_T = 0.96486 + 0.000162(T - 25) - 0.000002(T - 25)^2$$

This equation gives a value of  $+0.000190$  for  $dE/dT$  at  $18.00^\circ$ . Substitution of the values found in the Gibbs-Helmholtz equation gives  $Q = 46092[0.96363 - 291(0.000190)] = 41,867$  cals. Subtracting 582 cals. from this value as previously indicated gives the value 41,285 cals. as the free energy of the reaction  $\text{Pb} + \text{Hg}_2\text{SO}_4 \rightarrow \text{PbSO}_4 + 2\text{Hg}$ . This is an error of about 0.19%, when compared with the value obtained by Thomsen in a thermochemical way.

(b) The constancy of the voltage of a lead amalgam such as was employed in the preparation of the cell previously described, suggested that such an amalgam might be used in a measurement of the potential of the lead electrode, provided the difference in voltage between such an amalgam and a solid lead electrode were accurately known.

Several investigations of the lead electrode<sup>9</sup> have been made at various times but the data is not in agreement. Getman<sup>9</sup> describes a measurement of the potential of a solid lead electrode immersed in a saturated solution of lead chloride. This electrode was prepared by precipitating lead electrolytically upon platinum from a solution of lead nitrate. Fluctuations in voltage amounting to as much as 0.0022 volt were observed by Getman. It was thought possible that some action between the lead and the solution of the chloride might be taking place such as is the case in a solution of lead nitrate.

The plan of measuring the potential of lead against a solution saturated with lead sulfate and sodium sulfate appeared promising, judging from the constant results obtained in the standard cell. Several cells were accordingly prepared, identical in every respect with those described, except that a solid lead electrode was substituted for the amalgam. This solid elec-

trode was prepared by precipitating lead upon a heavy platinum wire according to the method described by Getman.<sup>9</sup> These cells while they did not agree exactly showed reasonable constancy for at least thirty hours after which a gradual decrease in voltage became apparent. The voltages follow:

TABLE V.

Cell I.	Cell II.	Cell III.	Cell IV.	Temp.	Time in hrs
0.96990	0.96967	0.96970	0.96972	25.00°	2
0.96991	0.96967	0.96971	0.96970	25.00°	5
0.96990	0.96968	0.96970	0.96970	25.00°	10
0.96990	0.96966	0.96970	0.96969	25.00°	18
0.96988	0.96965	0.96969	0.96969	25.00°	30

The mean of these values is 0.96974 volts. The voltage of a cell prepared with an amalgam instead of a solid electrode is 0.96463 volt. The difference between the two, 0.00511 volt, represents the potential difference existing between a solid lead electrode and a 3-4% lead amalgam.

The activity of the lead ion liberated by lead sulfate in a solution saturated with sodium sulfate would be very difficult to determine with any accuracy, and since this value must be known in order to calculate the normal electrode potential, the plan of measuring the potential difference between a 3-4% amalgam and a solution saturated with lead chloride was followed.

Since the solubility of lead chloride at 25.00° is 0.0388 mol. per liter, the activity of the lead ion may be determined with some degree of accuracy. At this dilution Noyes and Toabe<sup>11</sup> give the value of 56.2% for the extent of dissociation of lead chloride, but this result is based upon conductivity measurements, and may, therefore, be subject to a slight error. This error will not affect the accuracy of the measurements described, as a simple calculation will give the normal electrode potential, in case a revision of the activity of the lead ion is found necessary. Since this work was done an article has appeared by Lewis and Brighton,<sup>12</sup> in which they express the hope that they will be able to determine with greater certainty the activity of the lead ion at this dilution.

Attention was, therefore, directed toward the determination of the potential of a 3-4% amalgam of lead, against a saturated solution of lead chloride. All the measurements were made against a battery of three tenth-normal calomel electrodes. Some difficulty was experienced at first in preparing calomel electrodes that did not vary in voltage. Finally the preparation of calomel by the electrolysis of a normal solution of hydrochloric acid, using a mercury anode according to the method de-

scribed by Ellis,<sup>13</sup> produced calomel which gave excellent results in the standard electrodes. The calomel was washed free from hydrochloric acid by washing it in a Gooch crucible with a tenth-normal solution of potassium chloride, before being used in the cells. The potassium chloride used had been twice recrystallized and heated, and the solution was thoroughly saturated with calomel before use. No difference in potential was apparent between the three standards and each lead half-cell was measured against the three standards in turn.

The half-cell ( $\text{Pb}_2\text{Hg}-\text{PbCl}_2$  sat. solution) was prepared by covering the 3-4% amalgam of lead with about one cm. of solid lead chloride which had been recrystallized three times.

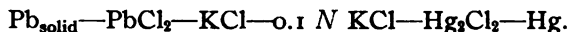
The cell was then filled with a solution of lead chloride saturated at about  $30.00^\circ$  thus insuring a saturated solution at  $25.00^\circ$  at which temperature all measurements were made. Connection with the standard electrode was made by means of a saturated solution of potassium chloride. These lead cells exhibited a very constant voltage during the sixty-hour observation period, though there was a slight difference between the different cells. The following values are the means of about ten measurements taken of the voltages of the cells during a sixty-hour period.

TABLE VI.

Voltage of the Chain ( $\text{Pb}_2\text{Hg}-\text{PbCl}_2-\text{KCl}-0.1 \text{ N KCl}-\text{Hg}_2\text{Cl}_2-\text{Hg}$ )

Amalgam I.	Amalgam II.	Amalgam III.	Amalgam IV.	Temp.
0.5138	0.5137	0.5135	0.5136	$25.00^\circ$

The voltage is indicated only to tenths of a millivolt because the resistance of the chain was large enough to make the fifth decimal uncertain. The mean of these values, 0.51365, is, therefore, taken as the voltage of the chain under consideration. Adding the value, 0.0051 volt, which is the difference in potential between the amalgam and a solid lead electrode, gives 0.5187 as the voltage of the chain



It is now possible to calculate the normal electrode potential of lead by means of the equation<sup>14</sup>

$$E = E^\circ - (RT/2F \ln C)$$

in which  $E = 0.5187$ ,

$E^\circ$  = normal electrode potential,

$R$ ,  $T$  and  $F$  have the usual values,

and  $C$  = concentration in mols. of lead ions present.

The degree of dissociation of lead chloride in a saturated solution is taken as 56.2% and the equation, therefore, assumes the following form:

$$0.5187 = E^{\circ} - RT/2F \ln (0.0388 \times 0.562) = 0.4696$$

This is the value of the normal electrode potential of lead measured against the tenth-normal calomel electrode at 25.00°.

## V. Summary.

A lead standard cell has been prepared which has been found to possess a constant voltage which is reproducible to within a few hundredths of a millivolt. The voltage of the cell is conveniently large to permit its use as a standard.

A determination of the potential of the lead electrode against the tenth-normal calomel electrode has been made and found to be 0.4696 at 25.00°. This value may be subject to a slight change when the activity of the lead ion in a saturated solution of lead chloride becomes more accurately known.

The author wishes to take this opportunity to thank Dr. William E. Henderson for his interest and his many timely suggestions.

## VI. References.

1. *Proc. Roy. Soc.*, **62**, 117.
2. Dissertation, O. S. U., 1916.
3. *Z. anorg. Chem.*, **36**, 201 (1903).
4. *Am. Chem. J.*, **25**, 216 (1901).
5. *Phys. Rev.*, **32**, 334 (1906).
6. *Ibid.*, **33**, 33 (1907).
7. *Z. phys. Chem.*, **56**, 645 (1906).
8. *Z. Elektrochem.*, **17**, 293 (1911).
9. (a) *Ibid.*, **7**, 477 (1900-01).
- (b) *Ibid.*, **10**, 77 (1904).
- (c) *Z. phys. Chem.*, **56**, 645 (1906).
- (d) *J. Chem. Soc.*, **38**, 792 (1916).
10. *J. Am. Chem. Soc.*, **25**, 469 (1903).
11. *Ibid.*, **39**, 1537 (1917).
12. *Ibid.*, **39**, 1906 (1917).
13. *Ibid.*, **38**, 737 (1916).
14. *Ibid.*, **35**, 1 (1913).

### ADDITIONAL REFERENCES.

- Z. Elektrochem.*, **2**, 681 (1905).  
 J. F. Spencer, "Ueber die electromotorische Wirksamkeit verdünnter Amalgame."  
*Am. Chem. J.*, **50**, 396 (1913).  
 C. N. Myers and S. F. Acree, "A Study of Calomel Electrodes."



*Z. phys. Chem.*, **47**, 146 (1904).

Ludwig Sauer, "Bezugselektroden."

*Z. phys. Chem.*, **35**, 333 (1900).

W. Ostwald, "Über die absoluten Potentiale der Metalle."

*Z. phys. Chem.*, **24**, 46 (1897).

T. W. Richards, "Ueber den Temperaturkoeffizienten des Potentials der Kalomelektrode mit verschiedenen gelosten Elektrolyten."

*Z. phys. Chem.*, **72**, 165 (1910).

T. W. Richards, "Elektrochemische Untersuchung flüssiger Amalgame."

*Trans. Am. Electrochem. Soc.*, **14**, 65 (1908).

G. A. Hulett, "Equilibria in Standard Cells."

### AUTOBIOGRAPHY.

I was born near Holland, Michigan, June 14, 1890. My early education was such as the country school afforded at the time. From 1904 to 1908, I was enrolled in the Hope College Preparatory Department, finishing the course in 1908. The following year I spent in the study of music at the Hope College Conservatory of Music. My interest in less artistic pursuits prompted me to enroll as a Freshman in Hope College, in September, 1909, and during that year I developed an interest in chemistry under the teaching of Dr. A. T. Godfrey, head of the Chemistry Department. I was graduated in June, 1913, receiving the degree of Bachelor of Arts. The next four years I spent in pursuit of the degree of Doctor of Philosophy at the Ohio State University, serving as an assistant in the Department of Chemistry while fulfilling the requirements of the degree which I received in June, 1917.

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